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# Oligomeric and polymeric surfactants for the transfer of luminescent ZnO nanocrystals to water†

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The water dispersion of luminescent nanocrystals (NCs) synthesized in organic solvent by encapsulation in a surfactant bilayer is a promising strategy for preserving the optical properties of NCs. The phase transfer of highly monodispersed ZnO NCs using the monomer, dimer, trimer and polymer of a series of alkyl ammonium surfactants is compared. Transfer yields over 60% could be obtained with the oligomers and the polymer. In contrast, we observed no measurable transfer using the single chain surfactant. NMR spectroscopy, including DOSY and NOESY, demonstrated that increasing the oligomerization number ameliorates the stability within the coating bilayer. The NCs exhibit a strong luminescence in water and show long term chemical and photo-chemical stability.



## Introduction

Inorganic nanoparticles with photoluminescent properties, referred to as quantum dots (QD), have numerous applications in the fields of sensing and imaging technologies. Various chemical and physical procedures were proposed for the development of new luminescent semi-conducting NCs, enabling access to a large variety of materials. The chemical methods are particularly appealing since they are more easily scaled-up and occur at lower temperatures than the physical methods. Some materials may be synthesized either in water or in organic solvent but so far, better shape control and higher crystallinity are obtained in organic solvents.[1]

We have previously evidenced the interest of organometallic synthesis for the preparation of metal oxide NCs.[2,3] In particular, luminescent ZnO NCs were synthesized by the reaction of an organometallic precursor with water at room temperature.[4,5] Crystal growth is controlled by ligands, typically an alkyl amine, yielding well-crystallized NCs whose size (typically 2–4 nm) can be tuned by the reaction conditions. These luminescent NCs appear to be good candidates for applications such as imaging due to their long term photo- and chemical stability, even under air exposure. However, the general drawback of organometallic procedures is that they yield NCs coated with a hydrophobic layer of alkyl ligands. An additional step is required to transfer the NCs to water when applications in aqueous media are targeted.

The most common strategy to convert hydrophobic nanoparticles to hydrophilic ones consists of the displacement of the original ligand by hydrophilic compounds.[6–9] For instance, gold nanoparticles are easily exchanged by grafting hydrophilic thiol ligands on the gold surface. However, these methods involve a strong alteration of the surface of nanoparticles which often results in the alteration of their optical properties.[10–12] In the case of ZnO, we have observed that quenching of the luminescence occurs when thiolated ligands are used.[13] An alternative strategy was proposed, based on the encapsulation of the nanoparticles within self-assembled aggregates of amphiphilic polymers or surfactants.[14–21] This strategy was successfully applied to QDs without changing their optical properties.[16,17] When surfactants are used, it is generally accepted that the added surfactant interacts with the pristine ligands *via* non-specific van der Waals interactions, forming an interdigitated double-layer of alkyl chains. This principle has been applied since the early 1980s for the stabilization of iron oxide particles prepared in water by co-precipitation. In this process, a primary surfactant – usually a fatty acid – is used to precipitate the

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particles. In a second step, a secondary surfactant is added, enabling the dispersion of the magnetic nanoparticles in water. Various single chain fatty acids, saturated as well as unsaturated, were successfully used in this context.[21,22] Another study also shows the re-dispersion of boehmite nanoparticles with hydrophobic coating using *n*-alkyltrimethylammonium bromide surfactants.[23] This process could in principle apply to all types of hydrophobic NCs and surfactants. Surprisingly, it was reported that alkyl chain-coated CdSe@ZnS quantum dots could not be transferred to water using single chain surfactants.[24] More generally, an attentive examination of the literature regarding the transfer of fluorescent quantum dots reveals that almost all successful procedures involve surfactants with 2–3 alkyl chains or polysoaps,[16,19,24–27] (to the best of our knowledge, there are only two exceptions[18,28]). Our group also observed that most single chain surfactants failed to phase transfer ZnO NCs protected by octylamine.[28]

In this context, the question of how the oligomerization of the surfactant affects the ability to form a bilayer-shell and the relationship with phase transfer seems an important issue. Previous studies have demonstrated that gemini (dimers) and higher order oligomers consisting of single chain surfactants connected by a spacer at the level of the polar headgroups display interesting features compared to their monomeric equivalents, such as very low CMC, high adsorption on solid surfaces, and a tendency to form bilayers.[29–34] Gemini surfactants were also found to be superior to their single-tailed analogues for solubilizing hydrocarbons in water.[29,35] They were recently used to control the growth and assembly of gold nanoparticles.[36–38]

In the present work, we compare the efficiency of surfactant monomer, dimer, trimer and polymer for the transfer of ZnO NCs to water NCsprepared with octylamine as the stabilizing ligand. The interaction between the added surfactant and the NCs was investigated using NMR spectroscopy. The optical properties (absorbance and luminescence) of the NCs after transfer to water were compared to the ones of the pristine ZnO NCs in organic solvent.

## Results and discussion

The hydrophobic ZnO NCs were synthesized following a well established organometallic procedure which has been previously described in detail (Fig. 1).[4] Octylamine (OA) is used as a stabilizing agent, yielding well-crystallized ZnO NCs of about 3–4 nm. A typical TEM picture of the isotropic NCs is displayed in Fig. 1. Interestingly, cyclohexane evaporates during the course of the reaction and no other by-products are formed. Therefore, OA is the only organic moiety present in solution after the synthesis. This facilitates the investigation of the stabilizing organic layer surrounding the NCs by NMR spectroscopy.

Among the various chemical structures of gemini described in the literature,[29,30,39] we selected the cationic alkyl-α,ω-bis(dimethylalkylammonium bromide) which was available in a series of monomers, dimers, trimers and polymers in order to investigate the influence of the degree of oligomerization on the transfer efficiency.[40] The oligomeric form is constituted of

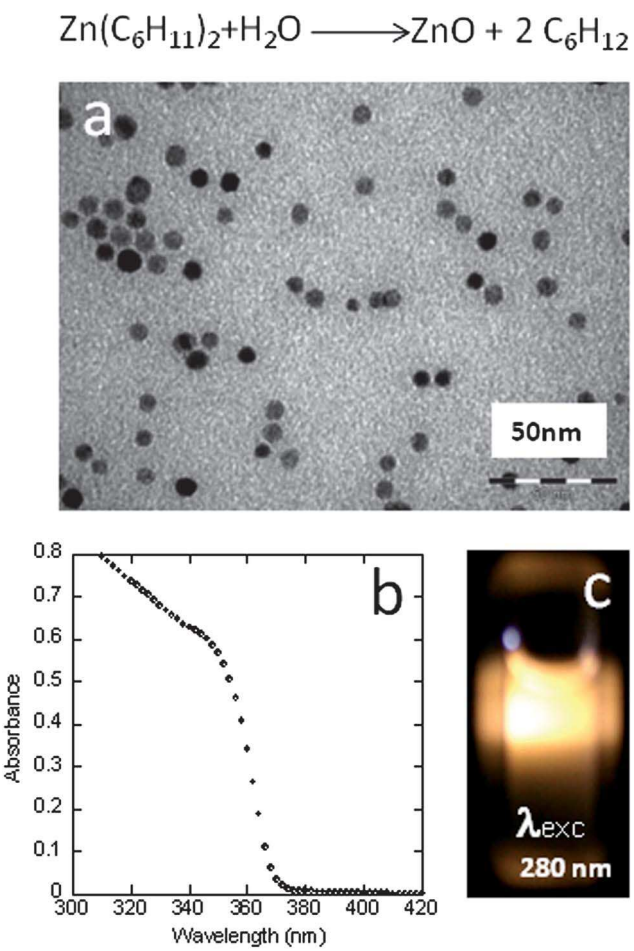


**Fig. 1** Top: reaction scheme of the decomposition of the organometallic precursor. (a) TEM pictures of the ZnO NCs; (b) absorbance spectra of isotropic NCs in dichloromethane; (c) photograph of the colloidal solution under UV irradiation.

alkylammoniums connected at the level of the ammonium polar head groups by a short spacer group (propyl). The polymeric form has a benzyl group between the ammonium and the spacer, but otherwise exhibits a very similar chemical structure

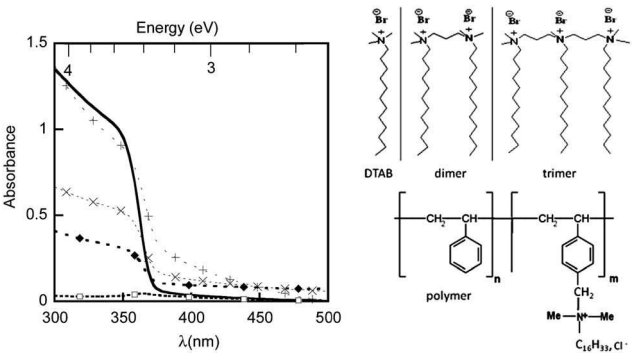


**Fig. 2** Absorbance measurements of the aqueous phases after the transfer procedure using the various surfactants compared to the absorbance of the pristine NCs in the organic solution before transfer. (—) Before transfer; (□) monomer = DTAB; (◆) dimer; (×) trimer; (+) polymer. Surfactant concentration: 2 mM.

**Table 1** Values of the CMC (in mM of alkyl chain); surface area per alkyl chain at the air–water interface ($a_M$); maximum adsorption of alkyl chains ($\Gamma_{max}$) and chain area at the silica–liquid interface of the surfactants used in this study

| | CMC[a] | $a_M$[b] (nm$^2$ per chain) | $10^6\Gamma_{max}$[b] molchain m$^{-2}$ | $A$[b] (nm$^2$ per chain) |
|---|---|---|---|---|
| DTAB | 15 | 0.59 | 3.5[b] | 0.95[b] |
| Dimer | 1.92 | 0.48[b] | 4.6[b] | 0.72[b] |
| Trimer | 0.48 | 0.49[b] | 5.25[b] | 0.63[b] |

[a] From ref. 43. [b] From ref. 40.

(Fig. 2). It is a statistical copolymer obtained by the copolymerization of styrene units and chloromethylstyrene units quaternized by a *N*,*N*-dimethylhexadecylamine.[41] The polymers contain on average 100 monomers, 80% of which bear an alkyl chain. In this respect, it can be considered as a long oligomer (*ca.* 80 alkyl chains) with spacers of variable lengths. The physical properties (critical micellar concentration, CMC; chain area at the air–water interface and chain area at the solid–liquid interface) of the surfactants used in this study are gathered in Table 1. All the "molar" units are expressed in terms of moles of alkyl chains. In comparison to their monomeric counterparts, the oligomeric surfactants aggregate at much lower chain concentrations. The relationship between the CMC and the free energy of micellization for surfactant oligomers was derived by Zana, and it appeared that the free energy of transfer of an alkyl chain from water to the micellar pseudophase is independent of the surfactant chemical structure.[42] The dimer and trimer with short spacer groups tend to form aggregates of reduced curvature such as threadlike micelles, as compared to DTAB which forms only spherical micelles even at high concentration.[40,43] However, close to the CMC, the aggregation number is only slightly higher for the oligomers, in the order DTAB < dimer < trimer. At a very low concentration, the polymer self-assembles in water within intramolecular aggregates which means that the CMC is not defined or can be considered to be equal to 0.

Due to the presence of OA, the pH of the solution after transfer was always close to the isoelectric point of ZnO in water (*ca.* 9) or higher.[44–46] The surface of the NCs was therefore positive or almost neutral so that no electrostatic interaction was expected with the cationic surfactants. In addition, the choice of a non-coordinating quaternary ammonium polar head group also prevents from specific interactions with ZnO. Thus, the choice of this family of surfactants enables one to investigate the formation of a double layer stabilized *via* van der Waals interactions only. In addition, the NCs transferred by this strategy were expected to maintain a luminescence in the visible range in water.

In most reported procedures, the new surfactant is added to an organic solution of the NCs, which are further precipitated and recovered as a powder of hydrophilic NCs.[16,24,47] However, precipitated NCs do not always readily redisperse. In order to avoid the precipitation step, we decided to transfer the NCs *via* an emulsion phase.[31] Typically, the new surfactant was dissolved in a concentrated dichloromethane solution of the ZnO NCs. Then, a small volume of this organic solution was added to water to reach a volumetric ratio of *ca.* 10%. The mixture was vigorously stirred in order to form an emulsion and the flask was left uncovered to allow for the evaporation of the dichloromethane. After evaporation of the organic solvent, a small amount of insoluble material could be observed on the wall of the vials, depending on the surfactant used and the transfer conditions. The amount of ZnO material transferred to water is determined from absorbance measurements at 350 nm.[28]

## Influence of the degree of oligomerization on the transfer yield

Fig. 2 compares the absorbances of the aqueous solutions using DTAB and the di- tri- and polymeric surfactants. The final concentration of alkyl ammonium chains in water ($C_{chain}$ = 2 mM) was kept constant for all experiments (2 equivalents relatively to octylamine). For instance, for the dimeric, trimeric and polymeric surfactant the value of $C_{chain}$ equals respectively: $C_{chain} = 2 \times C_2$; $3 \times C_3$ and $n \times C_n$, where $C_2$, $C_3$ and $C_n$ are the molecular concentrations of the dimer, trimer and polymer surfactant. From Fig. 2 it appears clearly that the single chain surfactant did not allow any significant transfer of the NCs. In contrast, the transfer was significant with the oligomeric and polymeric surfactants. To exclude any effect directly related to the presence or absence of micelles in solution, it was verified using DTAB and the other surfactants that single chain surfactants do not allow the transfer, even when used at concentrations over their CMC.[28] Importantly, the overall profiles and particularly the onset of absorbance of ZnO NCs (376 nm, 3.30 eV) were not modified by the transfer procedure. In all cases the yield of transfer was over 60% using the polymer as a transfer agent, which compares with the best results reported so far.[26,28] The trimers and dimers always exhibited transfer yields in the range of 50–90% and 20–80%, respectively. This large variation of the observed transfer yields for repeated transfer assays with the same surfactant was apparently related to different kinetics of the evaporation of dichloromethane, a difficult parameter to control. In addition, the aqueous solutions were sometimes slightly turbid, which makes it difficult to determine precisely the concentration of NCs from absorbance measurements in the UV range. Even though the polymer gave similar results to the trimer in terms of transfer, it exhibited the shortest colloidal stability on the long term (Fig. S2†). Indeed, in the presence of the polymer, a significant loss of absorbance (~20%) was observed within the first 24 hours whereas it took about 4 days in the case of the trimer. This decrease in stability may result from a slow photocatalytic degradation of the aromatic groups of the polymer, induced by ZnO.[48–50]

Our results demonstrate that increasing the polymerization number increases the transfer yield of these ZnO NCs, from *ca.* 0% for DTAB to more than 50% for the trimer and the polymer. These results are clearly consistent with other experimental work concerning the micellization, foaming, and oil solubilisation from oligomeric surfactants.[43,51,52] In all these situations, increasing the degree of polymerization promotes the molecular self-assembly. A full description of the reasons why

oligomeric surfactants aggregate more easily is not yet available because the driving force for the molecular assembly depends on a complex balance between repulsive interactions between neighbouring head groups and the attractive hydrophobic interactions between the hydrophobic tails. This latter arises primarily from the increase in the configurational entropy of water molecules released from the solvation zone of the hydrocarbon chains. However, thermodynamic measurements demonstrated that the low CMC of gemini results from their enthalpies of micellization (by unit of alkyl chain), more negative than those of their corresponding single chain surfactants.[53] The enthalpies of micellization and of adsorption on silica surfaces were also found to be more favourable for dimers than for monomers.[53–55] In the case of short spacers (as in this study), increasing the oligomerization number also reduces the effective size of the polar head groups, leading to more compact interfaces.[39,40,55] To summarize, both the ability to form molecular aggregates at low concentrations and their ability to form compact layers at interfaces may account for the observed transfer efficiency of the oligomeric surfactants.

Let us now consider the case of the polymer. Amphiphilic polymers bearing pendant alkyl chains are often referred to as "polysoaps" due to their analogy with micelle forming surfactants. Polysoaps have the ability to solubilize hydrophobic compounds in water. This property is related to the formation of intramolecular hydrophobic domains, or "intramolecular micelles". The conformation adopted by the polysoaps depends on molecular parameters such as their overall length and the proportion of alkyl chains.[56–59] The polymer used in this study was shown to form viscous and birefringent gel phases in concentrated solutions, as a result of the formation of long cylindrical aggregates.[41] In the present case, the polymer concentration was kept sufficiently low, in a non-viscous regime. Since the number of alkyl chains of one polymer (*ca.* 80) exceeds the typical number of surfactants within a conventional micelle (*ca.* 60), a simple view of the system is that in dilute solution one polymer would simply wrap around one nanocrystal,[60] thus allowing water solubilisation.

### Characterization of the organic coating by NMR spectroscopy

As demonstrated in previous work, NMR spectroscopy is a powerful tool to discriminate between the possible locations of the added surfactant, *i.e.* at the surface of the NCs, within surfactant micelles or free in the solution.[28,61] In order to investigate the state of the added surfactant, a direct transfer to $D_2O$ was achieved. NMR measurements were successfully achieved in the case of the monomeric and oligomeric surfactants. It was however not possible to retrieve significant information from NMR measurements when the polymeric surfactant was used. Thus, 6 types of samples were examined, *i.e.* for each of the 3 surfactants: (i) a reference sample consisting of a solution of the surfactant alone in $D_2O$ and (ii) the $D_2O$ solution resulting from the transfer procedure. $^1H$ solution NMR spectra measured after the transfer procedure were compared to the spectra of the corresponding surfactant alone in $D_2O$ (Fig. S3†). In the case of DTAB, no significant difference can be observed.

**Table 2** Diffusion coefficient of DTAB, and the di- and trimeric surfactant alone in $D_2O$ ("$D_{ref}$") and in $D_2O$ after the transfer procedure ("$D_{tran}$")

| | $D_{reference} \times 10^{10}$ $m^2\ s^{-1}$ | $D_{transfer} \times 10^{10}$ $m^2\ s^{-1}$ |
|---|---|---|
| DTAB | 4.0 (±0.5) | 3.5 (±0.2) |
| Dimer | 2.1 (±0.5) | 1.4 (±0.2) |
| Trimer | 0.6 (±0.2) | 0.3 (±0.1) |

In contrast, for the dimeric surfactant, the resonances corresponding to the protons in alpha positions of the amine head group, $\alpha$-$CH_2$ ($\delta$ 3.30) and $CH_3$ ($\delta$ 3.06), shift by 18 Hz and 15 Hz, respectively. The $^1H$ spectra of the trimeric surfactant are more complex with broad resonances and apparent duplication of several signals, suggesting that the trimer possesses different environments. However, broadening of the signals corresponding to protons in alpha positions of the amine head group (from 3.0 to 3.7 ppm) is observed after the transfer.

The diffusion coefficients of the surfactants were measured by DOSY (diffusion ordered spectroscopy). In solution, these surfactants can exist under states of different diffusion speeds (*e.g.* as free species, adsorbed onto the NCs surface or within micelles). If the exchange rate between these different states of the same molecule is slow compared to the time scale of NMR, then the diffusion coefficients corresponding to different states are observed separately. Conversely, in the case of fast exchange, an average coefficient is observed. In the present case, only single diffusion coefficients were observed (Table 2). The diffusion coefficient of the dimer in the reference solution is about half that of the monomer, consistent with the molecular size of the free species. Note that both species are mostly present as free species (no micelles) since the concentration is lower than the CMC (DTAB) or right at the CMC (dimer). In contrast, the much slower diffusion coefficient of the trimer showed that a significant amount of aggregates (micelles) is present in the reference solution. This is in agreement with the CMC values. After transfer, the diffusion coefficient decreased by a factor of 2 for the trimer. These values suggest that either the trimers are involved in larger aggregates in the presence of the NCs, or their residence time at the surface of the NCs is larger. In the case of the dimer, the diffusion coefficient, in $D_2O$, decreases from 2.1 (±0.5) $\times 10^{-10}$ $m^2\ s^{-1}$ to 1.4 (±0.2) $\times 10^{-10}$ $m^2\ s^{-1}$ in the presence of the NCs. This decrease suggests again that the dimer interacts with the ZnO–NCs. However, the diffusion coefficient remains larger than that for the trimer, indicating faster exchanges with the solution. A crude approximation of the number of dimers adsorbed on the NCs surface can be done. Indeed, the observed diffusion coefficient ($D_{transfer}$) is equal to $D_{transfer} = x_{free}\ D_{reference} + (1 - x_{free})\ D_{NCs}$, where $x_{free}$ corresponds to the molecular fraction of free dimers and $D_{NCs}$ to the diffusion coefficients of the nanoparticles.[61] Taking 2 nm as the radius of the inorganic NCs and 1.8 nm as the estimated thickness of an interdigitated mixed layer of octylamine and $C_{12}$ surfactant,[62] one can estimate the diffusion coefficient in water of the NCs: $D_{NCs} \sim 0.6 \times 10^{-10}$ $m^2\ s^{-1}$. Then, from the equation above: $x_{free} \sim 0.5$.

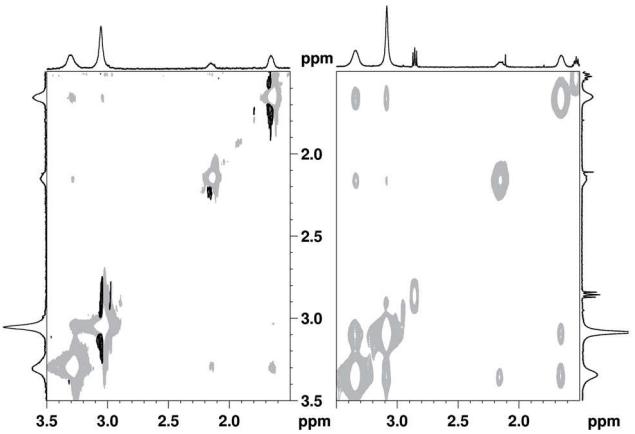


**Fig. 3** NOESY spectra (mixing time 100 ms) in $D_2O$ before (left) and after the transfer procedure (right) using the dimer.

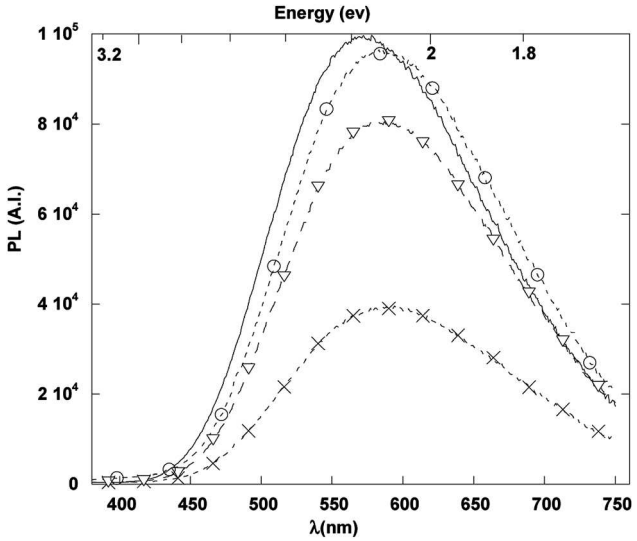


**Fig. 4** Emission spectra of ZnO NCs in dichloromethane (full line) and after transfer to water using oligo- and polymeric surfactants: (×) dimer; (∇) trimer, (o) polymer. $\lambda_{exc} = 340$ nm.

NOESY experiments (with mixing time of 100 ms) were also carried out for these 6 samples. DTAB showed predominantly zero quantum artifacts,[61] both for the reference sample and after transfer. In the case of the dimer (Fig. 3), the reference solution showed only very weak negative NOEs related to their small average size. After transfer, much more intense negative NOEs are observed. In the case of the trimer, negative NOEs are observed in the reference solution due to its average low mobility, as evidenced from its slow diffusion coefficient. The integration of the NOE cross peaks of the trimer showed that they increase to at least 50% after transfer. This increase of negative NOE amplitude after the transfer for the dimer and the trimer strongly suggests their interaction with the ZnO NCs.

In summary, for DTAB no significant difference could be observed by NMR spectroscopy, between the reference sample and the aqueous solution after the transfer procedure, in accordance with absorbance measurements showing that the NCs are not transferred. For the dimer, both the decrease in the diffusion coefficient and the increase in the negative NOE amplitude suggest that a significant fraction of the dimers is located at the NCs surface. However, the adsorbed dimers are in fast exchange with free species in solution. The slow diffusion coefficients together with the negative NOESY indicate that the trimer molecules are strongly adsorbed at the surface with a slow exchange rate with the solution. These results suggest that the dynamics of exchange between the double layer coating and the solution increases when the oligomerization number decreases. The mobility of the single chain surfactants may be responsible for droplet fusion and therefore NCs aggregation during the solvent evaporation process, preventing transfer.

### Optical properties of the ZnO NCs after their transfer to water

For the pristine NCs one main broad emission band is observed in the visible range centered at 580 nm (~2.14 eV) (Fig. 1). This yellow luminescence of ZnO NCs is frequently reported in the literature. It is generally admitted that it is caused by oxygen vacancies.[63,64]

Fig. 4 displays a comparison of the emission spectra before and after transfer for all the surfactants at $\lambda_{exc} = 340$ nm and shows that the NCs were also strongly luminescent in water. A small red shift of the emission maximum is systematically observed after the Ncs transfer as observed previously on transfer of the same NCs in water using other surfactants.[28] We believe that this red shift results from the quenching of some emitting surface defects. Indeed, the very broad emission band centered at 580 nm is most likely to be associated with different types of defects. The hydration of the Ncs surface may quench some of the defect emitting in the green region, leading to an apparent red shift of the band. In the case of the dimer and the trimer, we observed a significant loss of the emitted intensity (*ca.* −20%) in comparison to what is expected taking into account the transfer yield. In the case of the polymer, no significant quenching was observed. The origin of this quenching effect is still unclear. Some authors suggested that the quenching of the visible emission of ZnO may be caused by water molecules or hydroxyl groups, acting as electron donors.[48,64] Luminescence studies in the presence of various electron and hole scavengers also evidenced the role of the stabilizer in enhancing or retarding the quenching of ZnO NCs.[45] In any case, our results suggest that the polymer offers a better protective layer – steric or electrostatic – than its oligomeric analogues. The presence of longer alkyl chains (hexadecyl) and phenyl groups in the polymer may be responsible for the better protection of the nanocrystal surface toward water. The slower dynamics of the polymer might also play a role in its protective effect. Indeed, as indicated by DOSY measurements, the dimer and the trimer are in relatively fast exchange between the NCs surface and the solution. It can be expected that the polymer has much slower dynamics.

Importantly, the NCs could be transferred to a Tris buffer. Fig. 5 displays the absorbance of the colloidal solution of the ZnO NCs stabilized with the trimer in aqueous buffer: after 24 h,

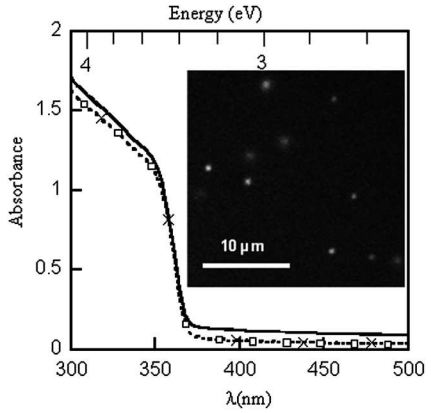


**Fig. 5** Time evolution of absorbance spectra of the ZnO NCs/trimer in a 0.7 mM Tris buffer: $t = 0$ (full line); after 15 h (□); after 24 h (×). Inset: fluorescence microscopy image of ZnO NCs in the buffer solution.



no sign of aggregation (light scattering) or degradation of the NCs could be observed. In addition, the luminescence emission remained stable under UV irradiation for several hours. Under a wide field fluorescence microscope the emission of the NCs is clearly observable as small distinct spots (Fig. 5).[65] Note that the choice of the buffer is crucial for the chemical stability of the NCs. For instance, the ZnO NCs were degraded in Hepes or PBS buffers within about 15 h.

## Conclusion

We compared the efficiency of mono-, di-, tri- and polymeric alkyl ammonium surfactants for the transfer of hydrophobic ZnO NCs to water, using the "interdigitated double layer" strategy. We observed that the dimer, trimer and polymer forms efficiently transferred the NCs, whereas the single chain surfactant DTAB could not. In addition, the trimeric and polymeric structures are more efficient than the dimeric one. From transfer assays and NMR spectroscopy we bring new experimental evidence that increasing the degree of oligomerization leads to more quantitative molecular aggregation at the NCs surface. The dynamics of molecular exchange between the double layer coating and the bulk seems to increase when the degree of oligomerization decreases, which most probably is the reason why DTAB could not transfer the NCs. The transferred NCs exhibited a strong photoluminescence in water. Importantly, the NCs are also stable in aqueous buffer – an essential step to envisage any biological application – and can be observed using a wide field fluorescence microscope, enabling prospects for use as cheap and safe photoluminescent labels.

## Experimental section

### Material

THF was purchased from Aldrich and purified by distillation before being used as a solvent for the synthesis of the ZnO NCs. The THF used to solubilise the NCs after the synthesis was not distilled.

### Synthesis procedures

Synthesis of the Zn precursor and the ZnO NCs were performed as described previously.[4] A THF solution containing (57.9 mg, 0.25 mmol) biscyclohexyl zinc and 1 eq. of octylamine was first prepared from freshly distilled THF in a glove box under argon. After extraction from the glove box, the solution was exposed to ambient moisture by opening the Schlenk tube. A powder is obtained after solvent evaporation, which readily dispersed into organic solvents such as dichloromethane. The NCs emit a yellow fluorescence on UV irradiation. A blue emission was also sometimes observed, which was previously attributed to the formation of imine groups.[65]

The dimer 12-3-12, 2Br has been prepared by quaternization of a commercially available tertiary diamine as previously described.[66] The surfactant trimer 12-3-12-3-12, 3Br has been synthesized by permethylation of the bis(3-aminopropyl)amine (norspermidine) followed by quaternization in acetonitrile:[40] a solution of polyamine in 3 M aqueous sulfuric acid and formalin (HCHO/N = 4) in an open flask cooled with an ice bath was treated with $NaBH_4$ ($NaBH_4$/N ≈ 2.5) at temperature below 15 °C. After several extractions with diethylether under acidic conditions, the permethylated amine was extracted with diethylether under basic conditions. The permethylated norspermidine was purified by distillation under vacuum (*ca.* 1 mm mercury) at 110 °C with an overall yield of 75%. Quaternization by dodecylbromide was carried out in dry acetonitrile at 30 °C for 3 days and completed at reflux for 2 hours. The raw surfactant thus obtained precipitated out upon cooling and addition of ethylacetate completed this process. The surfactant was recrystallized twice in the ethylacetate–ethanol mixture.

### Polymer synthesis

The polymer has been synthesized in two steps.[41] In the first one, a free radical copolymerization of 20 mol% of styrene and 80 mol% of vinylbenzyl chloride (both from ACROS) using AIBN (provided by Fluka) as the initiator proceeded in toluene until 60% of conversion. Considering the reactivity ratios of each comonomer and the overall composition of the copolymer, the latter is expected to display both a random-like microstructure and no drift in composition. The overall composition and the molar mass distribution of the precursor polymers have been respectively measured by $^1$H NMR spectroscopy and Size Exclusion Chromatography (SEC) in THF. The precursor chains contain 20 mol% of styrene units and have a number average molecular weight $M_n$ = 13.400 g mol$^{-1}$ and a polydispersity index PDI = 1.7. In a second step, a full quaternization of the VBC units polymer with *N*,*N*-dimethylhexyldecylamine (provided by Aldrich) is achieved in chloroform. The polymer consists of a polystyrene-like main chain bearing 80 mol% of amphiphilic pendants which are statistically grafted along the backbone.

### Transfer toward water

To the powder sample resulting from the synthesis, 6 mL of dichloromethane was added and the sample was stirred to yield

 

a transparent solution. A calculated amount of the desired surfactant was added to 4 mL of this nanoparticle solution, to reach a final concentration of 2 mM in alkyl chains. Then, 200 μL of this solution was added to 2 mL of water, forming an emulsion that was vigorously stirred. The vial was then opened to air under gentle stirring until evaporation of the dichloromethane was completed. The aqueous solutions were not filtered prior to optical measurements. Absorbance measurements were used for determination of the yield of transfer. A volume of 200 μL of the dichloromethane solution containing the ZnO NCs and the surfactant is added to 1.800 μL of dichloromethane to reach the same dilution as in water. Since the extinction coefficient of ZnO is the same in both solvents, the transfer yield is taken as the ratio of the absorbance of the aqueous solution to the dichloromethane solution (measured at 350 nm). For more details see ESI.†

### Optical characterization

All optical measurements were achieved using quartz cells of optical pathway 1 cm. Emission spectra were recorded using a Jobin–Yvon spectrofluorometer. NCs diluted in Tris buffer were observed through a Zeiss Plan Apochromat 63×/1.40 oil objective on a Zeiss Axioplan 2 microscope, using an X CITE 120 light source containing a mercury vapor short arc lamp (excitation filter 365/10, emission filter HQ595lp). Images were collected by a Cascade II 512 EM-CCD camera (Roper Scientific).

### NMR

For NMR samples the transfer procedure was achieved using $D_2O$ solutions of surfactants. 1D and 2D $^1H$ NMR experiments were recorded on a Bruker Avance 500 spectrometer equipped with a 5 mm triple resonance inverse *Z*-gradient probe. All chemical shifts are relative to TMS. All diffusion measurements were made using the stimulated echo pulse sequence with bipolar gradient pulses, at $T = 20$ °C. The 2D NOESY measurements were done with a mixing time of 100 ms.

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